

State Analysis of Electrolyte in Carbon Electrode for
Electric Double Layer Capacitor Studied
by ^{19}F NMR Spectroscopy.

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Electric double layer capacitor (EDLC) is one of promising candidates for the use in hybrid vehicles. As for EDLC, many studies have been made on electrolytes, solvents, separators and electrode materials^{1,2)}. EDLC performance should depend on the state of electrolyte in carbon electrode for which carbon is activated to give porosity, while a little study has been done on the state of electrolytes in carbon electrode³⁾. The objectives of our research are to establish the methodology for state analysis of electrolyte in carbon electrode and to clarify the state of electrolyte in carbon electrode.

Alkyl ammonium tetrafluoroborate is often used as electrolyte with propylene carbonate as solvent for EDLC. Taking into account to the fact that ^{19}F nucleus has a nuclear spin $I = 1/2$ and 100 % of natural abundance, ^{19}F NMR spectroscopy can be a powerful tool to investigate the state of electrolyte in carbon electrode by using BF_4^- as a probe.

In this work, we present the state analysis of BF_4^- in carbon electrode from the standpoint of interaction between BF_4^- and activated carbon surface. ^{19}F NMR chemical shifts reflect electronic structure of ^{19}F atoms and relaxation time $T_{2\text{F}}$ indicates their mobility. Therefore, these should be useful parameters to investigate the state of BF_4^- in carbon electrode.

The carbon electrodes were prepared from activated carbon powders with the variety of pore size. Tetrafluoroethylene was used as binder. The solution of triethyl-monomethyl-ammonium tetrafluoroborate salt (TEMA/BF_4) in propylene carbonate was soaked into the carbon electrode under the vacuum condition in the 5 mm Φ NMR sample tube. ^{19}F NMR spectra were measured with Jeol α -600 spectrometer at 564.67 MHz.

^{19}F NMR spectra are shown for the carbon electrode for which in Figure 1. Three peaks are observed with the chemical shifts at -151.5, -152.5 and -158.0 ppm in each spectrum except one. These three peaks are assigned to three states of BF_4^- , that is non-adsorbed, adsorbed on outer surface of carbon and on pore surface of carbon, respectively. ^{19}F NMR chemical shifts of BF_4^- , which adsorbed on pore surface of carbon, depends on its pore diameter. The relation between ^{19}F NMR chemical shifts of BF_4^- which adsorbed on pore surface of carbon and its pore diameter is plotted in Figure 2. It shows interaction between BF_4^- and pore surface changes in accordance with pore diameters.

Relaxation time $T_{2\text{F}}$ of BF_4^- is shown in Figure 3 for the carbon electrodes. Relaxation times $T_{2\text{F}}$ decreases for three states of BF_4^- in the order of non-adsorbed, adsorbed on outer surface of carbon and adsorbed on pore surface of carbon. It shows that adsorption to carbon surface makes the mobility of BF_4^- low.

$T_{2\text{F}}$ values of non-adsorbed BF_4^- and adsorbed BF_4^- on outer surface of carbon are independent with pore diameter of carbon. On the other hand, $T_{2\text{F}}$ values of adsorbed BF_4^- on pore surface of carbon increase in proportion to its pore diameter. This fact implies that the interaction between BF_4^- and pore surface of carbon decrease in accordance with increasing pore diameter.

Further, to investigate the state of TEMA^+ and propylene carbonate, ^{13}C NMR spectra were measured.

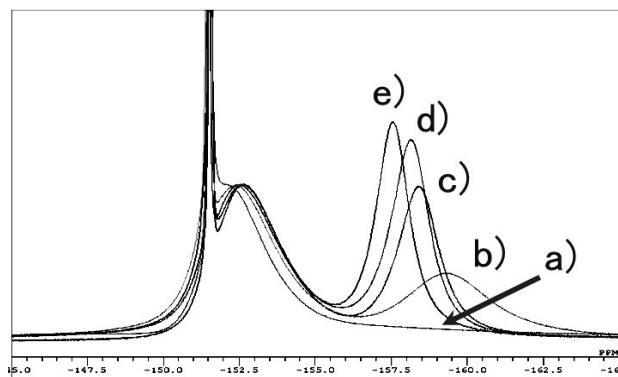


Figure 1 ^{19}F NMR spectra of carbon electrodes, which soaked with TEMA/BF_4 in propylene carbonate. Each carbon utilized in electrodes has different pore size. Pore diameter of each carbon is: a) 0.89nm, b) 1.01nm, c) 1.27nm, d) 1.43nm and e) 1.64nm.

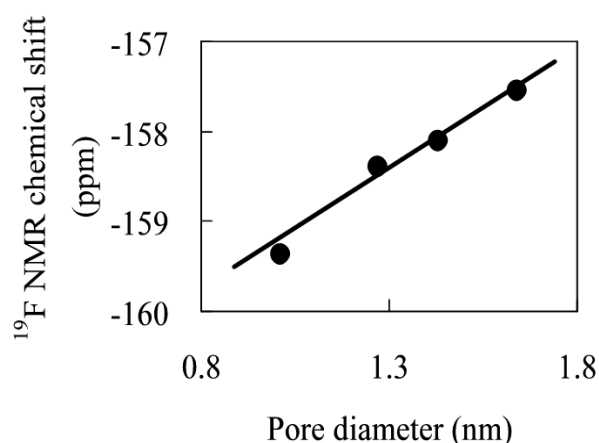


Figure 2 ^{19}F NMR chemical shifts of BF_4^- adsorbed on pore surface of carbon.

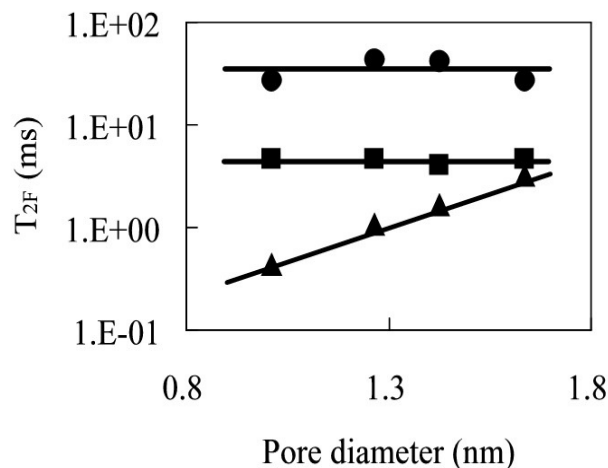


Figure 3 $T_{2\text{F}}$ of BF_4^- in carbon electrode.

● : not adsorbed, ■ : adsorbed outside pore of carbon, ▲ : adsorbed on pore surface of carbon.

References

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